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## DESCRIPTION

### RUBBER HOSE AND METHOD FOR MANUFACTURE THEREOF

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#### Technical Field

The present invention relates to an oil resistant rubber hose through which high-temperature gas passes and a method for manufacturing the same.

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#### Background Art

As is well known, in a vehicle, a rubber hose is connected between a turbocharger and an intercooler, and the intake gas pressurized by the fan in the turbocharger passes through this rubber hose. The fan is driven by the engine exhaust gas, so that the intake gas reaches a very high temperature. Accordingly, the rubber hose is required to have a heat resistance which can withstand such a high temperature and a vibration resistance at such a high temperature. As materials for such a rubber hose which is capable of withstanding the above mentioned high temperature, silicone rubber has hitherto been adopted. However, in current turbochargers, the pressurizing force is further increased, and consequently, the heat resistance required is such that turbochargers can withstand temperatures of 200°C or higher.

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In addition, the recent implementation of the Japan new short-term exhaust gas regulation of diesel vehicles also requires to install a positive crankcase ventilation system.

ATTACHMENT B

Accordingly, the above described rubber hose is also required to have an oil resistance and a resistance to gas permeation for the purpose of preventing the permeation of the blowby gas. For a rubber hose that is required to have such severe  
5 heat and oil resistance, conventional silicone rubber as used alone does not sufficiently meet these requirements, and rubber hoses made of new materials are demanded. In this connection, fluororubber attracts attention because it excels in heat resistance, oil resistance and the like, and an attempt has  
10 been made to produce a laminated air hose in which the fluororubber is used for the innermost portion thereof (for example, see Japanese Patent Laid-Open No. 2000-193152).

Japanese Patent Laid-Open No. 2000-193152 describes the structure of a laminated hose made of fluororubber and silicone  
15 rubber. However, it is difficult to obtain a hose having an oil resistance at high temperatures and a vibration resistance at high temperatures by simply combining individual materials on the basis of the properties of the respective materials. The critical points of this technique may include:

20 (1) a problem to develop a method for providing an adhesion, for withstanding the above described severe conditions, between fluororubber and silicone rubber which are chemically stable and hardly adhere with each other;

(2) a problem that fluororubber used in the innermost layer  
25 lacks flexibility due to its high rigidity; particularly, fluororubber has a common drawback that, under such high temperatures as ranging from 180 to 200°C which constitute

the application conditions of the turbocharger hose, fluororubber becomes brittle and tends to be broken, so that any material remedy may be hardly found and there occurs an issue about what structure is to be adopted;

5 (3) a problem that fluororubber has a significant drawback that it is high in crystallinity, and hence poor in brittle resistance at low temperature, resulting in generation of air leakage from the joint portions of the hose at low temperature; and

10 (4) a problem that fluororubber is a very expensive material, and hence it is critical from the economic viewpoint that the fluororubber layer is formed as thin as possible.

For the purpose of obtaining a practical hose, there are needed measures to comprehensively solve the above described  
15 problems (1) to (4), but no such measures are disclosed in the above described publication. In particular, the publication describes that the adhesion of fluororubber and silicone rubber to each other "is carried out by a conventional vulcanization adhesion," but it is impossible to adhere  
20 fluororubber and silicone rubber to each other by a conventional vulcanization method unless any special formulation is added to the rubber compounding.

#### Summary of the Invention

25 A first object of the present invention is to provide a novel rubber hose which has solved the above described problems and a method for manufacturing the rubber hose.

Another object of the present invention is to provide an improved rubber hose in which the low durability and low adhesiveness of the fluororubber layer is improved and upgraded by arranging a specific intermediate silicone rubber layer  
5 between the fluororubber layer and the outer silicone rubber layer.

A first aspect of the present invention is a rubber hose in which an outer rubber layer is laminated by means of extrusion on the outer peripheral surface of an inner rubber layer, the  
10 rubber hose being characterized in that:

the inner rubber layer is a fluororubber layer;

the outer rubber layer is a reinforcing yarn-woven silicone rubber layer having reinforcing yarns woven therein;

an intermediate rubber layer containing an adhesive  
15 component for the adhesion with the fluororubber layer is provided between the fluororubber layer and the reinforcing yarn-woven silicone rubber layer; and

the intermediate rubber layer is an intermediate silicone rubber layer having a hardness lower than those of the  
20 reinforcing yarn-woven silicone rubber layer and the fluororubber layer to be the innermost layer.

The fluororubber is preferably a terpolymer composed of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene or a copolymer composed of  
25 tetrafluoroethylene and propylene from the viewpoint of the resistance to the amines contained in the engine oil as an antiaging agent and an antirust.

The rubber hose according to the first aspect is preferably produced by the following manufacture method.

The method concerned is an extrusion method for manufacturing a rubber hose in which an intermediate silicone rubber layer having a hardness lower than that of the reinforcing yarn-woven silicone rubber layer is provided by means of extrusion between the fluororubber layer and the reinforcing yarn-woven silicone rubber layer outside thereof, the method concerned being characterized in that:

10       the fluororubber layer, the intermediate silicone rubber layer and the reinforcing yarn-woven silicone rubber underlayer are extruded in a laminated condition by a first extruder to be fed to a weaving machine;

15       the weaving machine weaves reinforcing yarns on the outer peripheral surface of the reinforcing yarn-woven silicone rubber underlayer and then feeds the laminate to a second extruder; and

20       the second extruder coats the outer peripheral surface of the reinforcing woven yarn with a reinforcing yarn-woven silicone rubber layer.

A second aspect of the present invention is a rubber hose in which an outer rubber layer is laminated by means of winding on the outer peripheral surface of an inner rubber layer, the rubber hose being characterized in that:

25       the inner rubber layer is a fluororubber layer;

      the outer rubber layer is a fabric-reinforced silicone rubber layer;

an intermediate silicone rubber layer containing an adhesive component for the adhesion with the fluororubber layer is provided between the fluororubber layer and the fabric-reinforced silicone rubber layer; and

- 5        the intermediate silicone rubber layer is an intermediate silicone rubber layer having a hardness lower than those of the fabric-reinforced silicone rubber layer and the fluororubber layer to be the inner layer.

The rubber hose according to the second aspect is  
10    preferably produced by the following manufacture method.

The method concerned is a winding method for manufacturing a rubber hose in which an intermediate silicone rubber layer having a hardness lower than those of the fabric-reinforced silicone rubber layer and the inner fluororubber layer is  
15    provided by means of winding between the fluororubber layer and the fabric-reinforced silicone rubber layer outside thereof, the method concerned being characterized in that:

the fluororubber layer sheet is prepared by use of a calendar roll;

- 20        the intermediate silicone rubber is press-coated (or, contact bonded) to the fluororubber layer sheet to prepare a laminated sheet composed of the fluororubber layer sheet and the intermediate silicone rubber layer sheet; and

the laminated sheet is wound around a metal mandrel having  
25    a predetermined shape, and then a fabric-reinforced silicone rubber topping sheet, prepared in advance, is wound on the laminated sheet to produce the rubber hose.

In this case, for the intermediate silicone rubber, a silicone rubber that is softer in the material hardness thereof than the fabric-reinforced silicone rubber is selected. The fabric-reinforced silicone rubber layer (hereinafter referred to as the silicone rubber layer) sheet as the topping sheet is a sheet in which an aramid reinforcing fabric or the like is incorporated in silicone rubber, and this sheet may be prepared by a conventional method in which silicone rubber is kneaded with a roll to be thermally plastic and then the silicone rubber is compression bonded with a calendar roll to either both or one of the surfaces of the fabric while a reinforcing fabric is being fed.

In the method for manufacturing the rubber hose in the second aspect according to the present invention, silicone rubber is extremely soft, so that it is very difficult to prepare a thin layer of approximately 0.1 to 0.3 mm in thickness if the silicon rubber is used alone, but actually, the laminated sheet composed of the fluororubber layer sheet and the intermediate silicone rubber layer sheet is prepared sequentially with a calendar roll, so that the softness of silicone rubber is compensated by the hardness of unvulcanized fluororubber, resulting in the improvement of the workability and the moldability. Consequently, there are also provided such advantages that the thickness of the fluororubber sheet can be made thin and uniform, and both sheets are compression bonded to each other under the conditions that soft silicone rubber is being thermally softened, so that the mutual adhesion

of both sheets is elevated and the air incorporated therebetween can be eliminated. According to this method, the fluororubber layer sheet can be made as extremely thin as 0.1 mm, so that this method is more favorable than the  
5 extrusion from the viewpoint of the cost.

As described above, fluororubber is hard and lacks flexibility, and in particular, when it undergoes large vibrations at high temperatures and stress concentration, it tends to be broken. Accordingly, when the intermediate  
10 silicone rubber layer composed of the silicone rubber having a hardness lower than those of the silicone rubber constituting the reinforcing yarn-woven (or fabric-reinforced) silicone rubber layer and the fluororubber constituting the inner fluororubber layer is provided between the fluororubber layer  
15 and the reinforcing yarn-woven (or fabric-reinforced) silicone rubber layer, the intermediate silicone rubber layer works as a shock absorber to disperse the stress exerted on the inner fluororubber layer. Also, the adhesion concerned is the one between the soft and same quality materials, as  
20 compared to the case where the fluororubber layer and the silicone rubber layer are directly adhered to each other, so that better adhesive force can be obtained. The adhesive component is needed to be mixed only in the intermediate silicone rubber layer, the mixed amount of the adhesive  
25 component can be made small in an economically efficient manner. Also, because fluororubber is poor in brittle resistance at low temperature, sealing properties at low temperatures are

lowered, for instance, when a counterpart pipe is inserted into the hose; however, the lamination of the intermediate silicone rubber layer excellent in brittle resistance at low temperature on such fluororubber layer improves the sealing  
5 properties.

#### Brief Description of the Drawings

Figure 1 is a schematic view illustrating an example of a rubber hose according to a first embodiment of the present  
10 invention;

Figure 2A is a schematic block diagram illustrating a preferable method for manufacturing the rubber hose shown in Figure 1;

Figure 2B is a schematic block diagram illustrating  
15 another preferable method for manufacturing the rubber hose shown in Figure 1;

Figure 3 is a schematic view illustrating an example of the rubber hose with ribs formed in the joining portion to a counterpart pipe, shown in Figure 1 or presented in a second  
20 embodiment shown in Figure 4;

Figure 4 is a schematic view illustrating an example of a rubber hose according to a second aspect of the present invention;

Figure 5 is a schematic block diagram illustrating a  
25 preferable method for manufacturing the rubber hose shown in Figure 4; and

Figures 6 and 7 each are a schematic view illustrating the embossment formed on the rubber hose shown in Figure 4.

#### Best Mode for Carrying Out the Invention

##### 5 (First Embodiment)

A rubber hose according to a first embodiment of the present invention will be described below with reference to Figures 1 to 3.

Basically, the rubber hose concerned is a rubber hose  
10 in which an outer rubber layer is laminated by means of extrusion on the outer peripheral surface of an inner rubber layer, wherein the inner rubber layer is a fluororubber layer 2, and the outer rubber layer is a reinforcing yarn-woven silicone rubber layer 1 with reinforcing yarns woven therein. The  
15 rubber hose has a structure in which an intermediate rubber layer 3 having an adhesive component for the adhesion with the fluororubber layer 2 is provided between the fluororubber layer 2 and the reinforcing yarn-woven silicone rubber layer 1, and the intermediate rubber layer 3 is an intermediate  
20 silicone rubber layer having a hardness lower than those of the reinforcing yarn-woven silicone rubber layer 1 and the fluororubber layer 2.

The basic matters of the rubber hose according to the first embodiment of the present invention are as described  
25 above, but when the following additional measures are applied, the functions and the properties of the rubber hose are further

elevated, and accordingly, the following measures will be described below with reference to Figures 1, 2A and 2B.

Such a rubber hose can be produced as described above by extrusion, and more specifically, the extrusion itself may  
5 adopt any common extrusion method. In other words, a central mandrel (not shown) is adopted for the purpose of ensuring the accuracy of the inside diameter and preventing the deformation of the unvulcanized rubber hose; the central mandrel is provided to any one of three extruders (only one  
10 of them is shown) actually constituting a first extruder 10, and thus the first extruder 10 extrudes, to the outer peripheral surface of the mandrel, the fluororubber layer 2, the intermediate silicone rubber layer 3 and the reinforcing yarn-woven silicone rubber underlayer 1a in a laminated  
15 condition.

A laminate extruded from the first extruder 10 is fed into a weaving machine 11, and the weaving machine 11 weaves heat resistant fiber such as aramid fiber on the outer peripheral surface of the reinforcing yarn-woven silicone  
20 rubber underlayer 1a as the outermost layer of the laminate. The types of the reinforcing yarn braiding with the braiding machine 11 may include various types such as braid, spiral and knit weavings, similarly to conventional cases. Extrusion is carried out while a silicone rubber upper layer  
25 1c is being laminated on the outer peripheral surface of the reinforcing woven yarn 1b. In this case, one or both of the reinforcing woven yarn and the silicone rubber upper layer

may be formed appropriately in multilayer forms according to the requirements involving pressure resistance and the like, similarly to conventional cases. The laminate continuously extruded is cut to a required length, the central mandrel is  
5 taken out, thereafter a mandrel for use in vulcanization is inserted instead to apply a predetermined vulcanization treatment and the like, and thus, a desired product is obtained.

In some cases, a silane coupling agent selected as an adhesive is applied onto the outer peripheral surface of the  
10 fluororubber layer 2. In this case, the extrusion of the fluororubber layer 2, the intermediate silicone rubber layer 3 and the reinforcing yarn-woven silicone rubber underlayer 1a by the first extruder 10 may be divided into two extrusions, namely, an upstream extrusion and a downstream extrusion, as  
15 shown in Figure 2B, in such a way that the fluororubber layer is extruded by an upstream, first extruder 10a, subsequently the silane coupling agent is applied thereon by a silane coupling agent applicator 13, and after the fluororubber layer is passed through a dryer 14, an extrusion operation of the  
20 intermediate silicone rubber layer 3 and the reinforcing yarn-woven silicone rubber underlayer 1a by a downstream, first extruder 10b may be carried out.

In the rubber hose thus produced, the thickness of the fluororubber layer required to be heat resistant and oil  
25 resistant is suitably 0.2 to 1.5 mm in consideration of the durability and the economic efficiency. The lower thickness limit of 0.2 mm is a limit due to extrusion, and may be of

the order of 0.1 mm if possible. Fluororubber is hard and lacks flexibility in nature, and further has a drawback that the strength thereof at high temperatures is weak. Under such conditions that, as described above, the temperature is as high as 200°C and vibrations are exerted, there is a fear that the tensile strength against elongation is degraded to cause failure. Also, when the fluororubber layer 2 is thinner than necessary, the rigidity of the rubber hose is increased by the hardening at low temperatures, and the sealing properties, the vibration-absorbing properties and the like are not able to exhibit their original performances. In order to solve such problems, the thickness of the fluororubber layer is critical, so that the above described range is appropriate.

Table 1 shows the results of the vibration endurance test (observation of the generation of cracks) at 180°C with variable thickness of various fluororubber layers 2; in any case, when the thickness exceeds 1.5 mm, the vibration endurance is degraded. In Table 1, ○ signifies no generation of cracks, △ signifies the generation of small cracks (0.05 mm or less in depth), and X signifies the generation of large cracks (more than 0.05 mm in depth).

Table 1

Thickness (mm)	0.2	0.5	1.0	1.2	1.5	2.0	2.5
Fluororubber A	○	○	○	○	○	X	X
Fluororubber B	○	○	○	○	○	△	X
Fluororubber C	○	○	○	○	○	△	X

Fluororubber A: Manufactured by Asahi Glass Co., Ltd. hardness (JIS A): 70

Fluororubber B: Manufactured by Sumitomo 3M Ltd. hardness (JIS A): 70

Fluororubber C: Manufactured by Daikin Industries, Ltd. hardness (JIS A): 70

It may be noted that, as the above described fluororubber, there was used any one of a terpolymer (fluororubber B or C) composed of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene and a copolymer composed of tetrafluoroethylene and propylene (fluororubber A).

The intermediate silicone rubber layer 3 which is provided between the fluororubber layer 2 and the reinforcing yarn-woven silicone rubber layer 1 (hereinafter referred to as silicon rubber layer 1) and functions as the shock absorber for these two layers has, as preferable conditions, a hardness lower than those of the silicone rubber layer 1 and the fluororubber layer 2. More specifically, the hardness of the intermediate silicone rubber layer is suitably lower by 10 to 30 in terms of the JIS A hardness. The thickness of the intermediate silicone rubber layer 3 is suitably 0.3 to 2 mm. For the purpose of making the intermediate silicone rubber layer 3 to take over the stress exerted on the fluororubber layer 2, the thickness of the intermediate silicone rubber layer 3 is

required to be 0.3 mm or more, but must not be too large and is suitably 2 mm or less. The thickness exceeding this is not preferable because such a thickness leads to the compression settling around the portion beneath the fastening band arranged along the outer peripheral surface of the silicone rubber layer 1. An adhesive component is mixed in the intermediate silicone rubber layer 3, and if the thickness thereof is increased, the mixed amount of the adhesive is also increased to raise the price. This is also another drawback.

It is also effective to mix aramid staple fiber in the fluororubber layer 2. Fluororubber is degraded in strength at high temperatures, and the mixing of such a heat resistant staple fiber makes it possible to prevent the strength degradation. Such a staple fiber attains anchoring effect to improve the adhesion. The mixed amount of aramid staple fiber is suitably 5 to 40 parts by weight in relation to the 100 parts by weight of the starting material polymer (hereinafter, this will be represented as "5 to 40 PHR"). When the mixed amount of aramid staple fiber falls outside this range, the above described functions are degraded. Examples of the usable aramid staple fibers may include aromatic polyaramids such as polyparaphenylene isophthalamide and polymetaphenylene isophthalamide.

It has been revealed that when silicone oil is mixed in the fluororubber layer 2, the elongation properties are improved, and the durability is also improved. As this silicone oil, (1) polymethylsilicone, (2)

polymethylphenylsilicone and the like can be used. The mixed amount of silicone oil is suitably 0.5 to 10 PHR. When the mixed amount is less than 0.5 PHR, the advantageous effect of silicone oil is small, while when the mixed amount exceeds 10 PHR, adhesion failure occurs. Thus, usually, the mixed amount is suitably 1 to 3 PHR. Table 2 presented below shows the relation between the mixed amount and the elongation index.

Table 2

	Fluororubber without silicone oil	(1) 3PHR	(2) 3PHR
Elongation index	100	130	150

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Mixing of magnesium oxide in the intermediate silicone rubber layer 3 is also preferable because this mixing improves the adhesion. In general, amine-vulcanized fluororubber and polyol-vulcanized fluororubber are mixed with magnesium oxide as acid acceptor; if magnesium oxide is also mixed in the intermediate silicone rubber layer 3, namely, a layer to be adhered, it can be seen that adhesion is improved. The mixed amount of magnesium oxide is suitably 2 to 15 PHR. When the mixed amount is less than 2 PHR, advantageous effects are small, while when the mixed amount exceeds 15 PHR, the intermediate silicone rubber layer 3 is hardened and unpreferably the durability is decreased. Table 3 presented below shows the relation between the mixed amount of magnesium oxide and the adhesion.

25

Table 3

Mixed amount (PHR)	0	2	10	15	20
Adhesion	X	△	○	○	Hardening failure

X: Interface failure; △: Partial interface failure; ○: Material failure

5 It has been found that in the case where the fluororubber layer 2 is of the peroxide vulcanization type, when triallyl isocyanurate is mixed in the intermediate silicone rubber layer 3, the adhesion strength is improved. The mixed amount thereof is suitably 1 to 15 PHR; when the mixed amount is less than 10 1 PHR, advantageous effects are small, while when the mixed amount exceeds 15 PHR, unpreferably scorch and viscosity increase are caused. Table 4 presented below shows the relation between the mixed amount and the adhesion depending on the fluororubber types. Here, the fluororubber types and 15 the evaluation symbols are the same as defined for Table 3 (also, the same as in Table 5).

Table 4

Mixed amount (PHR)	Unmixed	1	5	10	15	20
Fluororubber B	X	△	○	○	○	Hardened
Fluororubber C	X	○	○	○	○	Hardened

20 It has also been found that when a silane coupling agent is mixed in the intermediate silicone rubber layer 3, the adhesive force is increased. Such a silane coupling agent has preferably an organic functional group, such as an amino or epoxy groups. The mixed amount thereof is suitably 0.5

to 15 PHR; when the mixed amount is less than 0.5 PHR, advantageous effects are small, while when the mixed amount exceeds 15 PHR, unpreferably scorch is caused. Table 5 presented below shows the relation between the mixed amount of an aminosilane and the adhesion depending on the fluororubber types.

Table 5

Mixed amount (PHR)	Unmixed	0.2	0.5	2	5	10	15
Fluororubber B	X	X	△	○	○	○	Hardened
Fluororubber C	X	○	○	○	○	○	Hardened

When the rubber hose is practically used under the conditions that the temperature is as high as 200°C and additionally the rubber hose undergoes vibration, there occurs a phenomenon that the fluororubber layer 2 and the counter part pipe (not shown) connected to the hose are thermally fixed to each other to make the detachment thereof difficult. For the purpose of preventing such a phenomenon, it is effective to apply a release agent onto the inner peripheral surface of the fluororubber layer in the joining portion 2. This is because the application of a release agent reduces the dynamic friction coefficient to suppress the fixation. Among various release agents, silicone release agents are preferable because of the high releasing effect thereof. Because, for the purpose of attaining required functions to a full extent, this kind of hoses are usually subjected to post-vulcanization under conditions of about 5 hours at about 200°C, there is usually

adopt a procedure in which the release agent is applied with a brush or the like before this operation, and thermally fixed in the post-vulcanization.

Table 6 presented below shows a comparison of the detachment properties (anti-fixing properties) of the case where a release agent treatment was carried out by use of a baking-type silicone release agent HS-1 (manufactured by Toshiba Silicone Co., Ltd.) and the case where no such a treatment was carried out; the application of the release agent drastically improved the dynamic friction coefficient to permit detachment only by manual pulling.

Table 6

Anti-fixing properties		Dynamic friction coefficient
Not applied	X	1
Applied	○	0.3

X: Fixing is very strong, and detachment requires a release jig.

○: Detachable only by manual pulling

Conditions: A counterpart pipe made of aluminum was chosen, and a band fastening test was carried out at 200°C for 168 hours; thereafter, the fixing properties were evaluated.

As measures against the above described cracking, it is effective to provide ribs (see reference numeral 7 in Figure 3) along the circumferential direction in a protruding manner on the inner peripheral surface of the fluororubber layer in the joining portion 2. These ribs can be formed by use of a central mandrel with a rib-shaped end portion. When this

rubber hose is fastened by a fastening band, the fluororubber layer 2 is elongated along the longitudinal direction of the hose; however, if ribs 7 are provided in a protruding manner, the ribs 7 works as a compensation for the elongation, and  
5 the generation of cracks can thereby be prevented. The ribs 7 are provided along the circumferential direction, so as not to affect the sealing properties; when the number of the ribs 7 formed in this case is two or more, higher effects are attained. In addition, this structure reduces the contact surface area  
10 with the counterpart pipe, so as to be effective in preventing the fixation.

Table 7 presented below shows the results of the investigations of the generation of cracks when fastening is made with a fastening band by adopting a rubber hose in which  
15 a plurality of 0.5 mm high and 3 mm wide ribs 7 are formed in a protruding manner on the inner peripheral surface of the joining portion of the rubber hose and a rubber hose without such ribs. The effects of the application of the above described release agent were also simultaneously  
20 investigated; it has been found that the provision of the ribs 7 can suppress the cracking and the application of a release agent further improves the fixing properties. The fastening torque of the fastening band was set at 10 N-m; for an usual fastening torque of about 5 N-m, application of the above  
25 described procedures can suppress the cracking; thus, it is a very significant effect that the cracking and the fixation

were not caused even by applying such more severe and harsh fastening conditions as 10 N-m.

Table 7

	Ribs	Application of release agent	Cracking	Anti-fixing properties
Rubber hose (1)	None	No	Micro-crack ing	X
Rubber hose (2)	Present	No	No	○
Rubber hose (3)	Present	Yes	No	◎

5

In the evaluation of the anti-fixing properties in Table 7, the symbols "X and ○" are the same as described above, and the symbol "◎" means a condition in which detachment can be made only by manual pulling.

10

A method may be cited in which, for the purpose of ensuring the adhesion between the fluororubber layer 2 and the intermediate silicone rubber layer 3, an organosilane adhesive containing as the main component thereof a silane coupling agent is applied on the outer peripheral surface of the fluororubber layer in place of or in combination with the above described methods for improving the adhesion concerned. This application can be carried out automatically in the extrusion in such a way that the extrusion, by the first extruder 10, of the fluororubber layer 2, the intermediate silicone rubber layer 3 and the silicone rubber underlayer 1a is divided, as Figure 2B shows, into the extrusion of the fluororubber layer 2 by the upstream, first extruder 10a, the application

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of the silane coupling agent by the silane coupling agent applicator 13, and the extrusion of the intermediate silicone rubber layer 3 and the silicone rubber underlayer 1a by the downstream, first extruder 10b. According to this way, the  
5 adhesion between the fluororubber layer 2 and the intermediate silicone rubber layer 3 is improved. As the organosilane adhesive, Chemlock S-2, Chemlock S-10A, Megum 3290-1 and the like are used. These adhesives are available as alcohol solutions, a spray applicator may be used.

10 [Example 1]

There were produced a rubber hose (Y) and a rubber hose (Z) by use of the above described fluororubber B for the fluororubber layer 2, the rubber hose (Y) being provided with the intermediate silicone rubber layer 3 between the  
15 fluororubber layer 2 and the silicone rubber layer 1, and in the rubber hose (Z), the intermediate silicone rubber layer 3 being omitted to leave the silicone rubber layer 1 as only one silicone rubber layer. In the production of the rubber hose (Y), as shown in Figure 2A, a laminate composed of the  
20 fluororubber layer 2, the intermediate silicone rubber layer 3 and the silicone rubber layer 1 (JIS A hardness: 70) was produced by means of the method based on the first extruder 10, the <sup>braiding</sup>~~weaving~~ machine 11 and the second extruder 12. In  
the production of the rubber hose (Z), the intermediate  
25 silicone rubber layer was omitted. Here, each of the fluororubber layers was set at 0.3 mm in thickness; and the intermediate silicone rubber layer 3 had a JIS A hardness of

✓

50, contained magnesium oxide in a content of 5 PHR and triallyl isocyanurate in a content of 10 PHR, and was set at 1.0 mm in thickness. This extruded hose was cut to a predetermined length, the central mandrel was taken out, a bent mandrel for use in vulcanization which had an outside diameter of 50 mm and bellows was inserted, then the whole outer peripheral surface of the hose was wound with a heat shrinkable tape; the thus treated hose was placed in a boiler, and it was vulcanized at 165°C for 30 minutes to shape. After completion of the vulcanization, the tape was unwound and the hose was placed in a thermostatic oven to be subjected to a secondary vulcanization at 200°C for 5 hours for the purpose of attaining appropriate physical properties. The above described rubber hoses (Y) and (Z) produced in this way each were fastened with a band by exerting a torque of 5 N-m, and were subjected to a heat resistant durability test at 180°C, resulting in an observation that the rubber hose (Y) did not exhibit any abnormality, but the rubber hose (Z) exhibited cracks in the portion of the fluororubber layer 2 beneath the fastening band. Thus, the effectiveness of the intermediate silicone rubber layer 3 was confirmed.

As described above, in the rubber hose in which the fluororubber layer 2 and the silicone rubber layer 1 are laminated, when the intermediate silicone rubber layer 3 composed of a silicone rubber having a hardness lower than those of the silicone rubber constituting the silicone rubber layer 1 and the fluororubber constituting the fluororubber

layer 2 is provided between the fluororubber layer 2 and the silicone rubber layer 1, the intermediate silicone rubber layer 3 works as a shock absorber to disperse the stress exerted on the fluororubber layer 2; also because the intermediate  
5 silicone rubber layer 3 is soft, it enhances the adhesion with the fluororubber layer 2. Also, because the adhesive is needed to be mixed only in the intermediate silicone rubber layer 3, the mixed amount of the adhesive can be made small in an economically efficient manner.

10 (Second Embodiment)

A rubber hose according to a second embodiment of the present invention will be described below with reference to Figures 3 to 7.

As shown in Figures 4 to 7, the rubber hose according  
15 to the second embodiment is a rubber hose in which an outer rubber layer is laminated by means of winding on the outer peripheral surface of an inner rubber layer, the rubber hose having a structure in which the inner rubber layer is a fluororubber layer 5 and the outer rubber layer is a  
20 fabric-reinforced silicone rubber layer 4; an intermediate rubber layer 6 containing an adhesive component for the adhesion with the fluororubber layer 5 is provided between the fluororubber layer 5 and the fabric 4a-reinforced silicone rubber layer 4; and the intermediate rubber layer 6 is made  
25 to be a intermediate silicone rubber layer 6 having a hardness lower than those of the fabric-reinforced silicone rubber layer 4 and the fluororubber layer 5.

The basic matters of the second embodiment of the present invention are as described above, but when the following additional measures are applied, the functions and the properties of the rubber hose are further elevated. The  
5 details of the measures are as follows, being not much different from those described above for the case of the first embodiment.

The thickness of the fluororubber layer 5 required to be heat resistant and oil resistant is suitably 0.1 to 1.5 mm in consideration of the durability and the economic  
10 efficiency. Fluororubber is hard and lacks flexibility in nature, and further has a drawback that the strength thereof at high temperatures is weak. Under such conditions that, as described above, the temperature is as high as 200°C and vibrations are exerted, there is a fear that the tensile  
15 strength against elongation is degraded to cause failure. For the purpose of solving this problem, the thickness of the fluororubber layer is critical, and the above described range is suitable; as described above, in the winding method, the fluororubber layer 5 can be made to be a thin layer with a  
20 calender roll in such a way that a hose having a 0.1 to 0.5 mm thick fluororubber layer 5 can be produced advantageously in cost.

In addition to the above descriptions, the various experimental results (Tables 1 to 7) described in relation  
25 to the first embodiment and the descriptions associated therewith are also applicable to the case of the second embodiment. As described above, for the purpose of ensuring

the adhesion between the fluororubber layer 5 and the intermediate silicone rubber layer 6, available methods include a method in which an organosilane adhesive containing as the main component thereof a coupling agent is applied on  
5 the outer peripheral surface of the fluororubber sheet when a laminated sheet is produced by use of a calender roll; because this adhesive is available as an alcohol solution, the above purpose can be attained by uniform application thereof onto the fluororubber layer 5 sheet with a spray.

10 It is also preferable to form embossment as shown in Figures 6 and 7 when the outer peripheral surface of the fluororubber layer 5, facing the intermediate silicone rubber layer 6, is processed with a calendar roll. The fluororubber layer 5 is compatible with embossing, and the embossment  
15 formation thereon can be achieved with a common embossing. In this way, the surface area is increased and the anchoring effect of the embossment can also be expected to provide an effect that the adhesion between unvulcanized fluororubber and silicone rubber is increased and the adhesive force after  
20 vulcanization is thereby further increased.

Additionally, ribs 7 similar to the ribs (reference numeral 7 in Figure 3) formed in the first embodiment can also be formed on the fluororubber layer 5 of the second embodiment (see Figure 3). The fabrication method thereof and the  
25 operation and the advantageous effects thereof are the same as in the above described first embodiment.

The examples based on the second embodiment will be described below as Examples 2, 3 and 4.

[Example 2]

Performance tests were carried out on a rubber hose (Y) and a rubber hose (Z) in each of which the above described fluororubber B was used for the fluororubber layer 5, in the rubber hose (Y), a silicone rubber containing an amino silane in a content of 2 PHR and having a JIS A hardness of 40 for the intermediate silicone rubber layer 6, and in the rubber hose (Z), the intermediate silicone rubber layer 6 being omitted to leave the silicone rubber layer as only one silicone rubber layer. As shown in Figure 5, in the production of these rubber hoses, a fluororubber sheet is prepared (reference numeral 20), and the fluororubber layer 5 and the intermediate silicone rubber layer 6 were laminated with a calendar roll, resulting in a thickness of 0.2 mm for the fluororubber layer 5 and a thickness of 1.0 mm for the intermediate silicone rubber layer 6. The topping sheet for forming the silicone rubber layer was prepared as a 1.5 mm thick laminated sheet by press-coating (reference numeral 21) a silicone rubber having a JIS A hardness of 65 onto both surfaces of a meta aramid fabric. A laminated sheet composed of the fluororubber layer 5 sheet and the intermediate silicone rubber layer 6 sheet was wound around an iron bent mandrel which had an outside diameter of 85 mm and bellows, thereafter the topping sheet for the silicone rubber layer was wound triply (reference numeral 22), and then the whole outer peripheral surface of

the hose was wound with a shrinkable tape; the thus treated hose was placed in a steam chamber, and it was vulcanized at 165°C for 30 minutes. After completion of the vulcanization, the tape was unwound and the hose was placed in a hot-air oven  
5 to be subjected to a secondary vulcanization at 200°C for 5 hours for the purpose of attaining appropriate physical properties. The above described rubber hoses (Y) and (Z) produced in this way each were subjected to a durability test at 180°C, and the results obtained were compared. According  
10 to the results, the rubber hose (Y) did not exhibit any abnormality, but the rubber hose (Z) exhibited cracks in the portion of the fluororubber layer beneath the fastening band. Thus, the effectiveness of the intermediate silicone rubber layer was confirmed.

15 [Example 3]

Performance tests were carried out on a rubber hose (1) in which the above described fluororubber C was used for the fluororubber layer 5 and a silicone rubber having a JIS A hardness of 50 and containing magnesium oxide in a content  
20 of 7 PHR was used for the intermediate layer 6, and a rubber hose (2) in which no magnesium oxide was contained. In this case, the thickness of the fluororubber layer was set at 0.2 mm, the thickness of the intermediate silicone rubber layer was set at 0.5 mm, and the vulcanization and shaping of the  
25 topping sheet to be the silicone rubber layer and the hoses were carried out in the same manner as in above described Example 2. The above described rubber hoses (1) and (2) produced in

this way each were subjected to the same durability test as described above, and the results obtained were compared.

According to the results, the rubber hose (1) did not exhibit any abnormality over the whole area thereof, but the rubber hose (2) exhibited separation in a portion of the fluororubber layer 5 beneath the fastening band and in the ends of the hose. Thus, the effectiveness of magnesium oxide was confirmed.

[Example 4]

Two hoses were produced in the same manner as in Example 2; one was a hose in which a 0.2 mm thick layer of the above described fluororubber C (JIS A hardness: 60) was used for the fluororubber layer 5, a material (JIS A hardness: 45) in which a basic formulation further contained polymethylsilicone oil in a content of 3 PHR and magnesium oxide in a content of 10 PHR was used for the 1.0 mm thick intermediate silicone rubber layer 6, and a fabric-reinforced silicone rubber sheet (JIS A hardness: 65; total thickness: 1.3 mm) was wound therearound in triple layers, and the other was a hose which did not include the intermediate silicone rubber 5.

On these two hoses, a low-temperature seal durability (at -40°C, with repeated cycles of the internal pressure variation from 0 to 250 kPa) test was carried out with 50 g of an engine oil placed inside each of the hoses. Consequently, without the intermediate silicone rubber layer 5, oil bleed leakage was caused from the end portions, but with the intermediate silicone rubber layer 5, absolutely no leakage

was found. Thus, the low-temperature drawback of fluororubber was compensated by the intermediate-layer silicone rubber which is excellent in brittle resistance at low temperature and has flexibility, and consequently  
5 excellent properties were able to be attained.

As described above, also in the case of the rubber hose according to the second embodiment in which the fluororubber layer 5 and the silicone rubber layer 4 were laminated, similarly to the above described first embodiment, placement  
10 of the intermediate silicone rubber layer 6 between the fluororubber 5 and the silicon rubber 4, where the intermediate layer is composed of a silicone rubber having a hardness lower than those of the silicone rubber constituting the silicone rubber layer 4 and the fluororubber, enables the intermediate  
15 silicone rubber layer 6 work to as a shock absorber, disperse the stress exerted on the fluororubber layer 5, and make the fluororubber layer of the hose thinner. The intermediate silicone rubber layer 6 enhances the adhesion with the fluororubber layer 5 to result in an enhancement of the adhesion  
20 of the layers by an adhesive, and the adhesive is needed to be mixed only in the intermediate silicone rubber layer 6, the mixed amount of the adhesive can be made small in an economically efficient manner.